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Abstract: Spark plasma sintered zirconia (3Y-TZP) specimens have been produced of 140 nm 372 nm and 753 nm grain sizes by sintering at 1250 □C, 1450 □C and 1600□C, respectively. The sintered zirconia specimens were grinded using a diamond grinding disc with an average diamond particle size of about 60 µm, under a pressure of 0.9 MPa. The influence of grinding and annealing on the grain size has been analysed. It was shown that thermal etching after a ruff grinding of specimens at 1100 □C for one hour induced an irregular surface layer of about a few hundred nanometres in thickness of recrystallized nano-grains, independently of the initial grain size. However, if the ground specimens were exposed to higher temperature, e.g. annealing at 1575 °C for one hour, the nano-grain layer was not observed. The resulted grain size was similar to that achieved by the same heat treatments on carefully polished specimens. Therefore, by appropriate grinding and thermal etching treatments, nanograined surface layer can be obtained which increases the resistance to low temperature degradation.

Dear Dr. Pietro Vincenzini
General Editor
Ceramics International

Many thanks for accepting the manuscript ref "CERI-D-16-03294" for publication in Ceramics International. We are enclosing the manuscript with the changes suggested by reviewers.

Yours sincerely,
Latifa Melk

*Cover Letter

Dear Editor

In this manuscript, we studied the effect of grinding on 3Y-TZP sintered using Spark Plasma Sintering (SPS) at three different SPS temperatures 1250 °C, 1450 °C and 1575 °C which induces different grain sizes 140 nm, 372 nm and 753 nm respectively. The surface microstructural changes on the grain size after grinding and annealing were investigated.

To the best of our knowledge, this is the first time, the microstructural changes after grinding zirconia sintered by SPS is studied .The current study showed that a thermal etching at 1100 °C after grinding the samples induces a surface layer of recrystallized nanograins in the range of few hundred nanometers. However, the annealing of ground specimens at high temperature results in high grain sizes similar to that achieved by the same heat treatment on polished specimens.

We hope you find this manuscript interesting and worth publishing

Best regards

Latifa Melk

Surface microstructural changes of Spark Plasma Sintered zirconia after grinding and annealing

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Abstract

Spark plasma sintered zirconia (3Y-TZP) specimens have been produced of 140 nm 372 nm and 753 nm grain sizes by sintering at 1250 °C, 1450 °C and 1600°C, respectively. The sintered zirconia specimens were grinded using a diamond grinding disc with an average diamond particle size of about 60 μm, under a pressure of 0.9 MPa. The influence of grinding and annealing on the grain size has been analysed. It was shown that thermal etching after a ruff grinding of specimens at 1100 °C for one hour induced an irregular surface layer of about a few hundred nanometres in thickness of recrystallized nano-grains, independently of the initial grain size. However, if the ground specimens were exposed to higher temperature, e.g. annealing at 1575 °C for one hour, the nano-grain layer was not observed. The resulted grain size was similar to that achieved by the same heat treatments on carefully polished specimens. Therefore, by appropriate grinding and thermal etching treatments, nanograined surface layer can be obtained which increases the resistance to low temperature degradation.

Keywords: zirconia; SPS; grinding; annealing; grain size; low temperature degradation

1 Introduction

Yttria stabilised tetragonal polycrystalline zirconia (3Y-TZP) has a wide range of applications, especially in the medical sector, because of its biocompatibility and very good mechanical properties, such as strength and toughness. The local and constrained phase transformation from tetragonal (*t*) to monoclinic (*m*) structure generates compressive stresses at the crack tip which enhances toughness. However, 3Y-TZP suffers from surface spontaneous *t-m* transformation in humid atmosphere, often referred to as hydrothermal degradation, aging or low temperature degradation (LTD), which is accompanied by formation of near surface microcracks and loss of surface mechanical properties [1–4].

During the processes of final shaping and surface finishing, 3Y-TZP may be subjected to different machining processes (cutting, polishing, grinding, and milling). The damage induced by machining affects structural integrity and reliability of the material. Therefore, machining zirconia is considered as a critical step in the manufacturing of long lasting and strong 3Y-TZP components.

Previous investigations have shown that grinding influences the surface integrity and the flexural strength of 3Y-TZP materials [5]. Therefore, most of the studies on ground zirconia have focussed on characterizing surface microstructural changes that may affect the chemical and mechanical behaviour. The main changes frequently observed in the X-ray diffraction (XRD) spectrum are the following: (1) *t–m* phase transformation; (2) asymmetrical broadening of the (1 1 1) tetragonal peak at ≈30° (2θ); (3) intensity reversal of the tetragonal doublet at 34.64° and 35.22° (2θ) corresponding to the (0 0 2) and (2 0 0) planes [6–10]. On the other hand, a TEM investigation of the ground surface by Munoz et al. [11] reported the existence of three different regions from the ground surface towards the bulk : (1) a recrystallized zone, exactly at the surface, where the grains have a diameter in the range 10–20 nm; (2) a plastically deformed zone; (3) a *t-m* transformed zone, which is mainly responsible for the formation of compressive residual stresses that usually increase the flexure strength and the apparent fracture toughness of ground specimens [11].

The near surface monoclinic phase formed during machining operations can be reversed to tetragonal by annealing. The operation of grinding and the time and temperature of annealing have an influence on the resistance to LTD, which can be inhibited or delayed [12]. The evolution of the resistance to LTD of specimens

of initially 330 nm grain size subjected to grinding and annealing at 1200 °C for different times (1 min, 10 min and 1h) was analysed by Muñoz et al. [13]. The results showed that LTD of ground 3Y-TZP was supressed due to the formation of a recrystallized nano-grain layer on the surface. Moreover, the resistance to LTD was decreasing during long time annealing at 1200 °C after that grain size reached grew beyond the initial surface grain size of 330 nm. The effect of different high annealing temperatures in the range 1200°C - 1600°C on the surface microstructure of ground zirconia was recently studied by Roa et al. [14]; they also found the recrystallized surface nano-grain layer after annealing at 1200 °C by milling a small cross section of the near surface region by FIB/SEM, while at 1600 °C the near surface microstructure was composed of larger grain sizes than the grain size of the bulk material.

To the best of our knowledge, previous studies of the effect of grinding has been carried out only on 3Y-TZP with grain size around 330 nm sintered using conventional methods. However, the aim of this work is to study the of surface microstructural changes after grinding and annealing on grains in the range of 140-370 nm produced by Spark Plasma Sintered (SPS) at 1250 °C and 1600 °C, respectively.

2 Experimental

2.1 Material processing

Zirconia powder stabilized with 3 mol % of yttria (TZ-3YSB-E, Tosoh, Tokyo, Japan) with a crystalline size of 36 nm was sintered using spark plasma sintering (SPS) at 1250 °C, 1450 °C and 1600 °C for 5 minutes. The pressure maintained during the sintering cycle was 55 MPa and the heating rate was 100 °C/min.

The final samples were ceramic discs (50 mm x 3 mm). The average grain size was determined using the line intercept method on SEM images and the density was measured by the Archimedes method**.**

The samples were ground using a new diamond grinding disc (MD-Piano 220 Struers) with an average particle size of about 60 μm, under a pressure of 0.9 MPa with a constant grinding speed of 3.6 m/s in one direction and water cooling. The selection of this grinding condition was based on a previous work of Juy et al. [15], who found that these particular parameters produce an increase in mechanical properties. The samples were then thermally etched at 1100 °C for 1

hour in standard furnace in air in order to observe grain size in the scanning electron microscope (SEM).

The samples studied will be referred to as SPS 1250, SPS 1450 and SPS 1600 according to the temperature used for sintering at 1250 °C, 1450 °C and 1600 °C, respectively. The samples were divided into two batches. The first batch corresponds to the as-ground samples which are referred in the current study as GRD (as ground). In order to reveal the grain size of the GRD samples, they were maintained at 1100 °C for 1 hour for thermal etching, 1200 °C for annealing, and at 1575 °C for high temperature annealing. The second batch consists of specimens that were polished starting with 9 μm diamond down to 1 μm and finally polished with colloidal silica. The polished samples were subjected to the same heat treatment temperatures, and are herein referred to as POL (as polished). In fact, each heat treatment on ground and polished specimens was carried out on the very same sample by polishing one face of the disc and grinding the other face in order to ensure that both faces were exactly subjected to the same temperature during annealing.

2.2 Mechanical testing

Hardness was measured by Vickers indentation with a load of 98.1 N. The cracks emanating from the vertex of the residual impressions were used to measure indentation fracture toughness using Niihara equation [16] taking into account the observed Palmqvist configuration of the indentation cracks. Anstis et al. [17] equation was also applied for comparative purposes. However, as extensively reported in the literature [18], indentation fracture toughness does not really represent the "true" fracture toughness (K_{Ic}) of the material. Therefore, the fracture toughness measurements in the present work have been used only as an indication of *t-m* transformability under localised sharp contact of compressive loads.

2.3 Surface Analysis

The crystallographic phases were identified by X-ray diffraction (XRD) with Bragg-Brentano symmetric-geometry, using PANalytical Empyrean equipment with PIXcel-3D detector and Cu-Kα (45kV and 40mA) radiation. The XRD spectra were obtained in a scan range of 20° ≤2θ≤ 100°, using a step size of 0.013° and an

anti-scatter slit of 1°. The monoclinic phase content was calculated by the equation proposed by Toraya et al. [19].

$$V_m = \frac{1.311 \times (I_m^{(\bar{1}11)} + I_m^{(111)})}{1.311 \times \left(I_m^{(\bar{1}11)} + I_m^{(111)}\right) + I_t^{(111)}}$$

Surface damage analysis of all the specimens was performed by extreme high resolution scanning electron microscopy (XHR-SEM) (Magellan 400, FEI Company) at an acceleration voltage of 3 kV. Microstructural changes below the surface induced during the grinding process were investigated by preparing thin cross-sections using focused ion beam (FIB). Cross sectioning observations were conducted using a dual beam workstation (Zeiss Neon 40). A thin platinum layer was deposited on the sample prior to FIB with the aim of reducing ion-beam damage. A Ga+ ion source was used to mill the surface at a voltage of 30kV. Final polishing of the cross-section was performed at a current of 500 pA.

3 Results and discussion

Table 1 shows clearly that the use of SPS results in dense zirconia samples of about 99% of theoretical density. SPS is a highly efficient technique for the densification of zirconia ceramics compared with conventional sintering such as Hot Pressing (HP) for example. Self-heating from spark discharge between the particles could be the reason behind the low temperature and short time for sintering. It has been found that during SPS the residual gases in the powder will be efficiently removed as long as the system is open. As the pressure will not be applied until the isothermal temperature is reached, CO_2(g) and H_2O(g) can then escape before the densification starts [20].

Furthermore, by increasing the SPS temperature, the grain size increases from 140 nm to 750 nm for SPS 1250 and SPS 1600, respectively, see **Table 2** and **Fig. 1**. It has been reported that the presence of an electric field could enhance the grain growth in yttria-stabilized cubic zirconia by increasing the grain boundary mobility [21]. Moreover, a dependency was shown between grain size and the heating-rate which promoted grain growth by increasing the defect concentration [22].

Fig. 2 shows the XRD spectra of GRD in all SPS zirconia samples. It can be observed the presence of a broadening of the tetragonal peaks and that the tetragonal peak at 2θ≈30° that corresponds to $(111)_t$ has a ~~s~~peak shoulder that

may correspond to either the rhombohedral phase or to distorted tetragonal phase as was reported in [14]. The presence of monoclinic phase at 2θ≈ 28, 16° was also observed. It has been found that the monoclinic phase detected in GRD is 13 %, 14 % and 12 % for SPS 1250, SPS 1450 and SPS 1600 respectively, see **Fig. 3**.

After annealing at 1200 °C and 1575 °C, the peak shoulder disappears and no monoclinic phase is detected due to the *m-t* transformation that actually starts at lower temperatures [23]. It could also be observed that the intensity of (002) and (200) tetragonal peaks at 2θ=34, 64° and 35,22° is reversed compared to the POL. In POL, the intensity ratio of $I_t^{(002)}/I_t^{(200)}$ is equal to 0.45 while in GRD annealed at 1575 °C, $I_t^{(002)}/I_t^{(200)}$ the ratio is equal to 1.63. This is attributed to the texture due stress induced reorientation from ferroelastic domain switching [7].

Indentation fracture toughness is similar to that for conventionally sintered 3Y-TZP with similar grain size, independently of the indentation equation used for calculating the fracture toughness. On the other hand, there is a small decrease in hardness with grain size which may be related to a higher transformability as the grain size increases, see **Table 2**.

The specimens GRD with subsequent thermal etching at 1100 °C for 1 hour show a nanometric grain size on the surface as can be seen on the images of left column of **Fig. 3**. The larger grain size observed in GRD was always much smaller than the average grain size in POL. After thermal etching at 1100 °C, the grain size in the GRD was reduced by a factor of 2 compared to the POL in SPS 1250 and by a factor of 10 in SPS 1575. However, if GRD specimens are annealed at 1200 °C or 1545 °C, the surface grain size increases fast and it reaches dimensions roughly similar to as POL specimens subjected to the same high temperature treatment. This can be appreciated by comparing GRD and POL specimens under the same heat treatment (see **Fig. 3**).

The analysis of sections perpendicular to the surface obtained by FIB (**Fig. 4**) shows that there is a very thin layer of surface damage on GRD specimens after grinding. The layer extends to depths of only a few hundred nanometers. The depth is not uniform and it changes from one place to another. It is deeper close to places where the material is piling up at the side of the grinding scratches. The same observation was carried out after annealing and they are shown in **Fig. 5**.

Fig. 5 shows the presence of the nano-grain layer with a depth corresponding to the same depth of the nano-grain layer seen in the ground specimens before annealing.

The existence of this surface nano-grain size layer on thermal etched GRD specimens can also be detected on the fracture surface of specimens as shown in **Fig. 6** where the fracture surface of POL and GRD are compared. The presence of nano-grain layer in the etched GRD specimens can be clearly observed. This nano-grain layer is formed by recrystallization of a very thin highly deformed surface layer produced during grinding. Since the usual procedure to observe the grain size is by means of grinding with decreasing diamond particle size and careful polishing, the damage layer is finally removed so that no recrystallization is detected during standard specimen preparation and thermal etching for grain size determination.

In one of the earliest investigations on this topic [12], it was shown that this recrystallized nanometric layer can be useful for preventing hydrothermal degradation because the resistance to LTD increases as the zirconia grain size decreases. The requirement of a smooth polished surface for many applications makes this procedure feasible when a specular smooth surface finish is not required. It may be of interest when a rough surface is beneficial as for example for implants since roughness favours osseointegration [24].

Regarding the influence of the surface damage induced by grinding on the strength, it was shown that it does not affect the strength of ground specimens. On the contrary, grinding induces the formation of a compressive surface layer which results in an increase of the strength [25,26]. However, after thermal etching and recrystallization, the compressive forces disappear as monoclinic phase is transformed back to tetragonal and then the strength may slightly decrease depending on the damage induced by grinding [11].

It is still unknown how much minimum plastic deformation by grinding is needed in order to form nanocrystals during etching. It will be interesting to find out which are the weakest grinding conditions for which recrystallization still takes place during thermal etching. **Fig. 7** shows a shallow scratch left on a polished surface where recrystallization still takes place in and around the scratch. This shows that the recrystallization could still remain after polishing if a deep

scratch is not fully removed by subsequent operations of grinding with smaller particle size followed by polishing.

4 Conclusions

Spark plasma sintered 3Y-TZP specimens have been produced with different grain sizes of 140 nm, 372 nm and 753 nm by sintering at 1250 °C, 1450 °C and 1600 °C. The influence of grinding and annealing has been analysed. Two main conclusions can be derived from the present work: a) the effect of the grinding conditions used in this study induces a few hundred nanometer surface layer which recrystallizes during thermal etching at 1100 °C. The surface layer contains recrystallized nano-grains with a grain size smaller and practically independent of the initial grain size depending on the SPS temperature. This behaviour is similar to that of conventionally sintered zirconia specimens; b) if the ground layer is exposed to higher annealing temperatures, the nano-grain layer disappears and the surface grains grow to a size which is similar to that achieved in polished specimens by heat treatment to the same temperature. The nano-grain layer formation could ~~inhibits~~inhibit the low temperature degradation.

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Table captions

Table 1. Density and grain size of the SPS zirconia specimens before and after annealing.

Table 2. Vickers hardness and indentation fracture toughness of the SPS zirconia samples.

Table 1

		Temperature/Grain size					
Specimen	Density ($g.cm^{-3}$)	1100°C POL (nm)	1100°C GRD (nm)	1200°C POL (nm)	1200°C GRD (nm)	1575°C POL (nm)	1575°C GRD (nm)
SPS1250	6.00 ±0.03	140±10	59±7	144±16	105±9	611±93	602±153
SPS1450	5.99± 0.09	372±50	66±15	386±29	149±22	699 ±79	896±167
SPS1600	6.05± 0.04	753±60	67±11	658±76	±	856±57	708±97

Table 2

Specimen	Vickers hardness (HV10) (GPa)	Indentation K_{IC} (Niihara) ($MPa \cdot m^{1/2}$)	Indentation K_{IC} (Anstis) ($MPa \cdot m^{1/2}$)
SPS 1250	14.7±0.2	5.2±0.1	3.9±0.2
SPS 1450	13.8±0.1	5.1±0.1	3.8±0.1
SPS 1600	13.6±0.2	5.2±0.1	4.0±0.1

Figure captions

Fig. 1 SEM images showing the microstructure of POL after thermal etching at 1100 °C for 1h: **a)** SPS 1250 **b)** SPS1450 and **c)** SPS1600.

Fig. 2 XRD spectra of SPS zirconia POL, GRD, GRD+annealed at 1200 °C and GRD+annealed at 1575 °C.

Fig. 3 Grain size of GRD SPS specimens after thermal etching for 1 hour at the temperatures indicated on the top row.

Fig. 4 Microstructure of GRD below the surface **a)** SPS 1250; **b)** SPS1450 and **c)** SPS 1600 after grinding and before thermal etching.

Fig. 5 Microstructure of GRD after thermal etching **a)** SPS 1250 top left **b)** SPS1450 top right **c)** SPS 1600 bottom after grinding and thermal etching.

Fig. 6 Fracture surfaces of POL (top) and GRD (bottom) SPS1250. General views on the left and high magnification details of the surfaces on the right.

Fig. 7 Surface of polished SPS 1450 after etching at 1100 °C with the initial grains and the recrystallized grains which appear in scratches still left on the surface after polishing.

Figure 1

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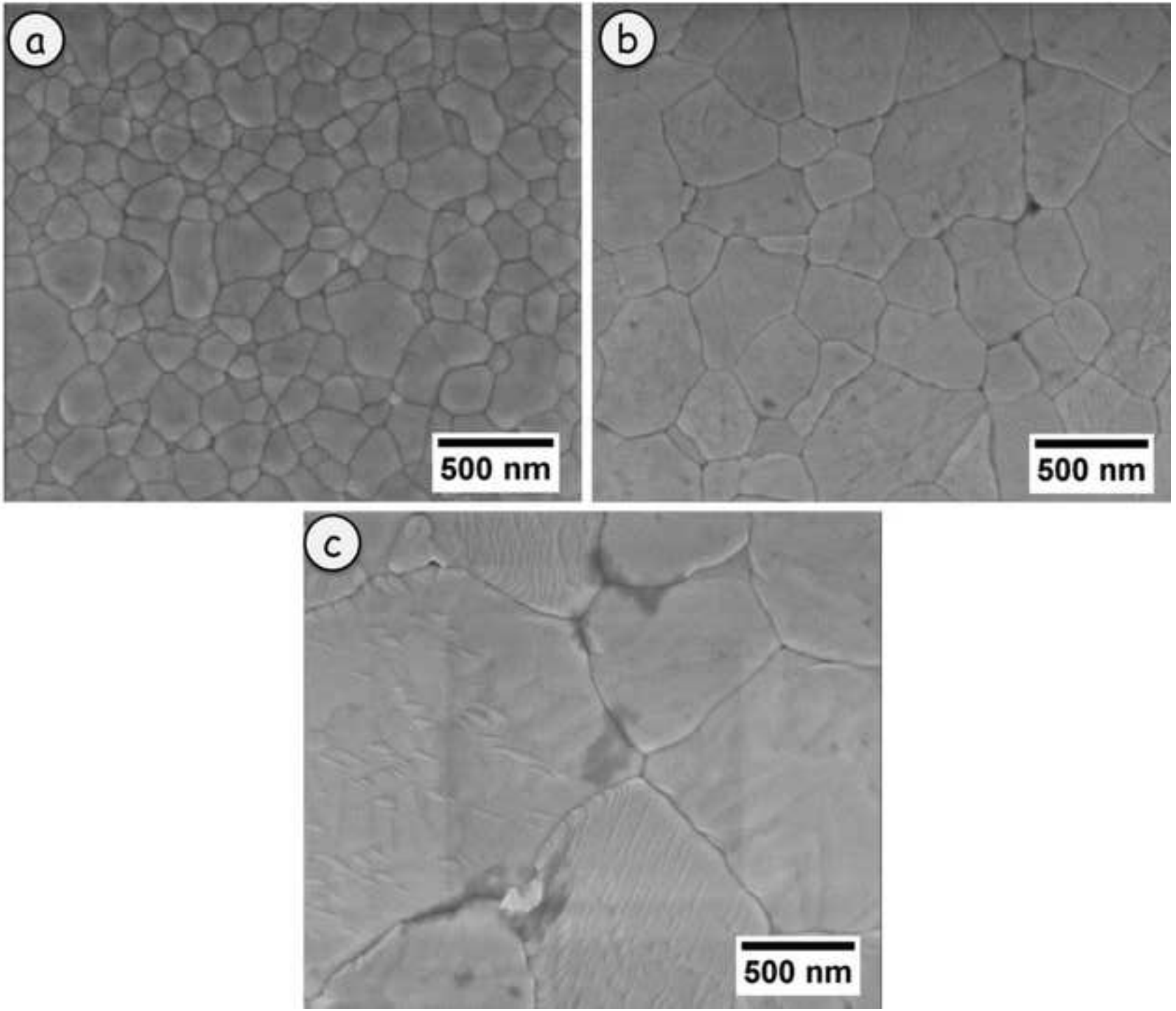

Figure 2

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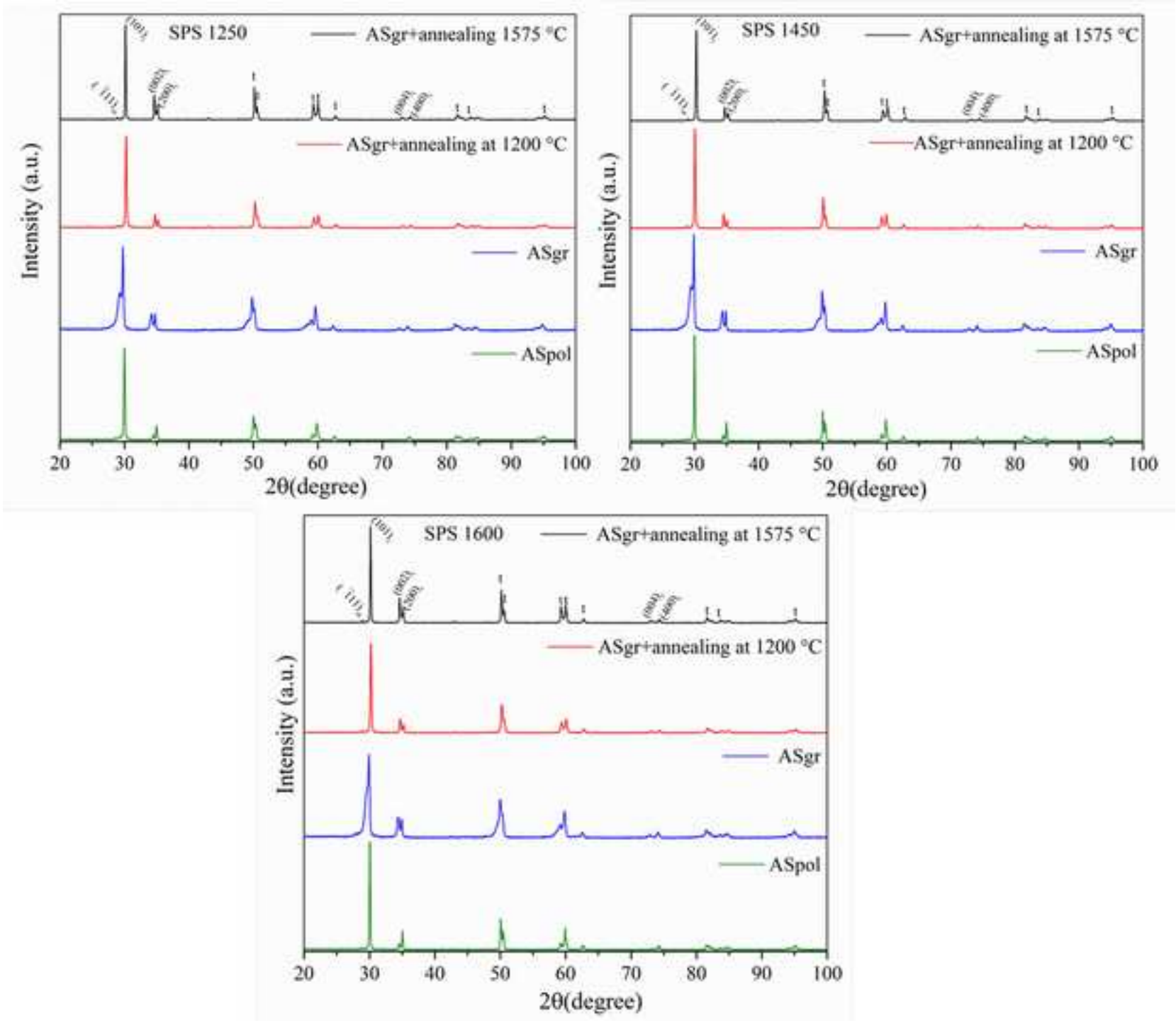

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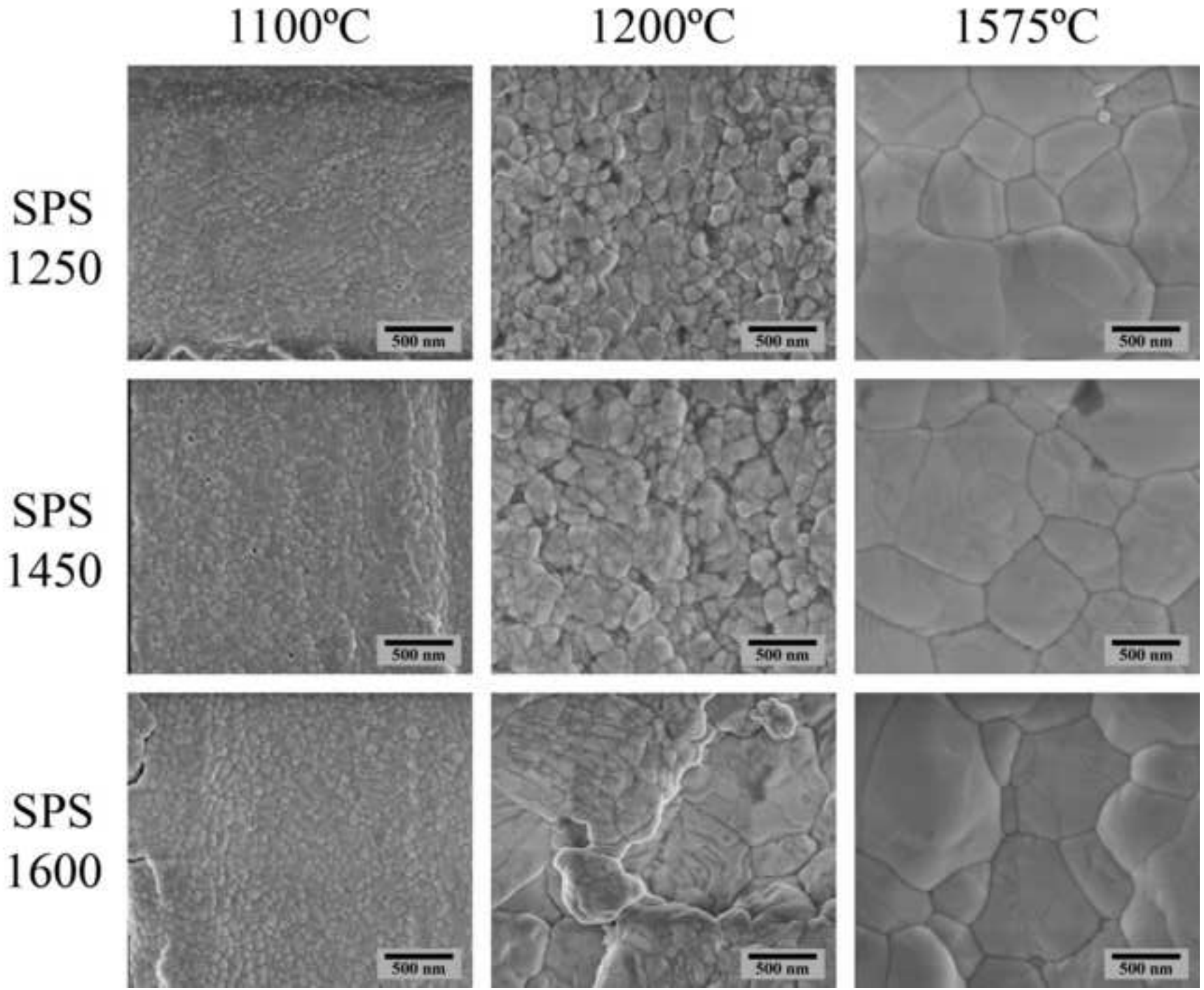

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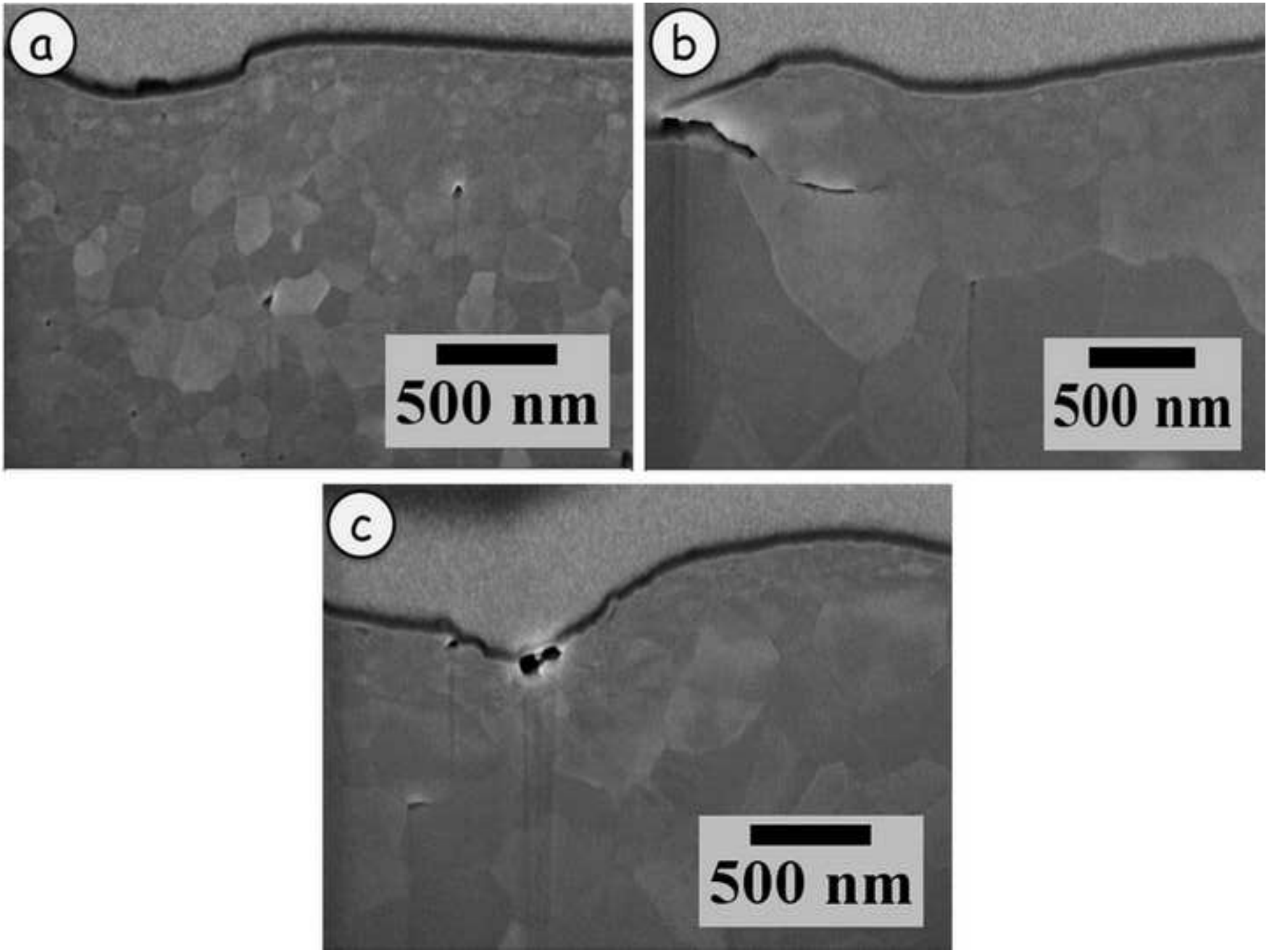

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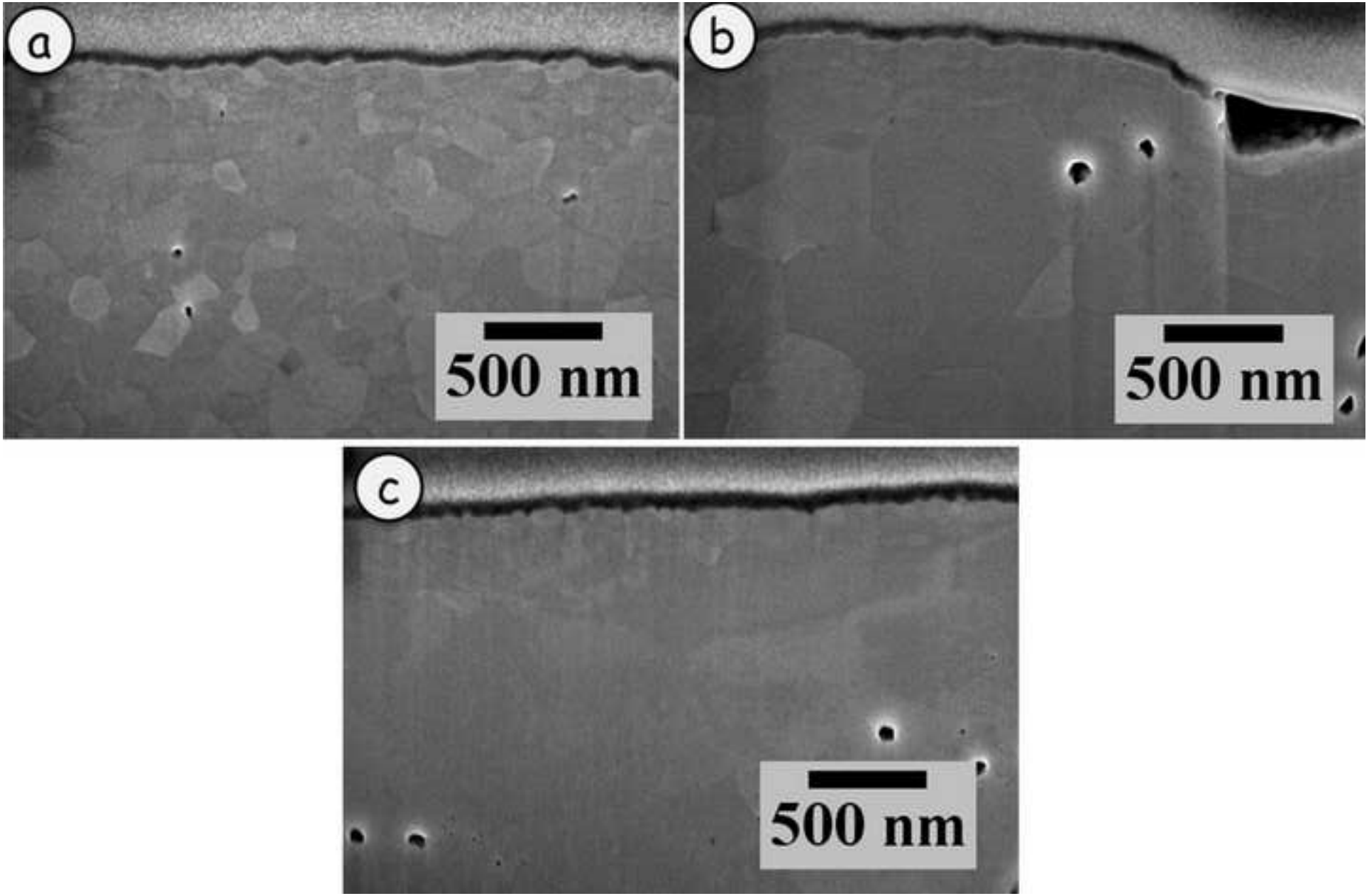

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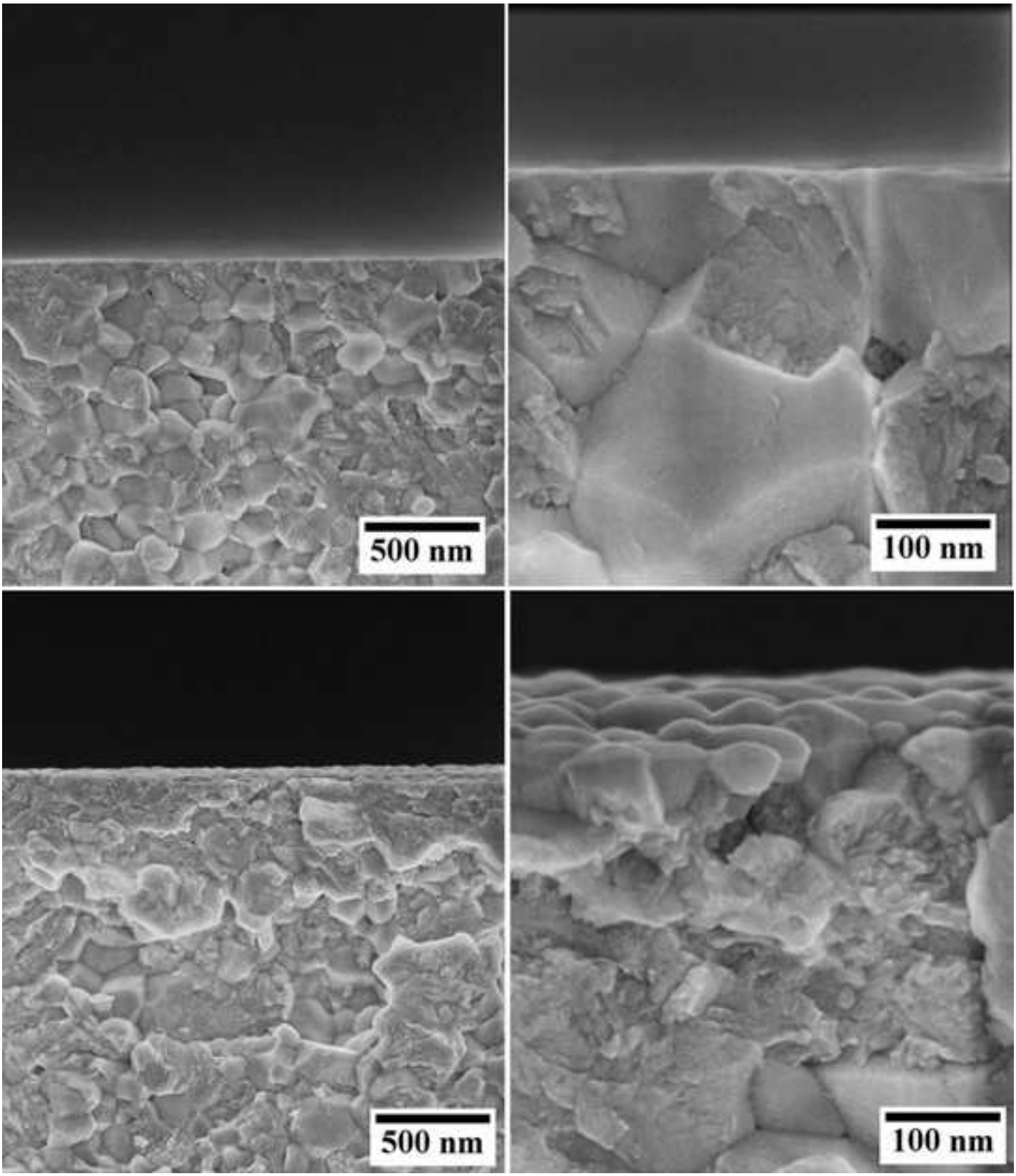

Figure 7

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